



Radioisotopic investigation of the oleic acid-1-¹⁴C HDO reaction pathways on sulfided Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts

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ARTICLE INFO

Article history:

Received 7 July 2014

Received in revised form

22 September 2014

Accepted 30 September 2014

Available online 8 October 2014

Keywords:

Natural triglycerides

Hydrodeoxygenation

Biofuel

Catalyst

Radioactive method

ABSTRACT

Oleic acid labeled with radioactive carbon at the carboxyl group (oleic acid-1-¹⁴C) has been applied to follow the hydrotreating process (reactions) of this compound over Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts, treated with H₂S. The aim of the present study was to expose the transformation of the carboxyl group, including its splitting from the oleic acid, on two catalysts of substantially different chemical content.

A flow-system catalytic reactor equipped with a special unit for microanalysis was applied for the study of the decarboxylation, decarbonylation and hydrodeoxygenation reactions at atmospheric pressure in the stream of hydrogen gas of different rates in the temperature range of 573–673 K. The gas products contained only ¹⁴CO, ¹⁴CO₂ and ¹⁴CH₄. One of the alkanes among the products formed in the hydrodeoxygenation process (C₁₈H₃₈) was also radioactive. No radioactive products were detected among the alkanes with carbon number <18. The ratio of $\sum C_1$ formation the $\sum C_1$ products from the oleic acid conversion was lower, than that of the C₁₇H₃₅¹⁴CH₃ produced. This is explained by the higher energy barrier, i.e. activation energy value, required for the dissociation of the C–C bond on the catalysts—being an inevitable condition of the formation of ¹⁴C₁-products—than that of the ¹⁴C–O bond dissociation on these catalysts, required for the transformation of ¹⁴COOH + 1/2H₂ → ¹⁴CO₂ + H₂O.

It is stated that at the applied conditions, only small amounts of sulfur leave the ³⁵S-labeled sulfided catalyst samples, consequently the sulfur loss of the samples can influence the catalytic behavior of these samples only after a longer period.

The experiments serve for a general conclusion: the radioactive microanalytical method based on the application of oleic acid-1-¹⁴C, is suitable for testing and evaluation of new catalyst samples in hydrotreating process of natural triglycerides.

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1. Introduction

In the last decade bio-fuels have obtained higher and higher importance. Mostly bio-ethanol made from starch or sugar containing crops by fermentation, and biodiesel produced from vegetable oils by trans-esterification are used straight or in blends with fossil fuels. Regarding the feedstock and production technology these represent first generation bio-fuels. Although they have no or very low greenhouse gas emission potential, as presented in Fig. 1 [1], the feedstock and crop land requirements for these fuels are in direct competition with food production, consequently questions of sustainability may be arisen. Accordingly, new, advanced

biofuels need to be produced from non-food feedstock such as used fats, other lignocellulose materials or waste products.

Such a technology is the hydrotreatment of waste oils and fats. Biogas oils, i.e. the mixtures of normal and isoparaffins can be produced by catalytic hydrotreating of natural triglycerides (fats and vegetable oils) on sulfided nickel and/or cobalt promoted molybdenite-alumina catalysts containing often some phosphorous [2]. Hydrogen is applied in this process to remove oxygen from triglycerides and fatty acids. Hydrotreating has previously been studied [2–4] for converting fatty acid and fractions of tall oil and other vegetable oils into straight chain alkanes (n-C₁₅–C₁₈).

Intensive studies have been carried out in this field to determine the optimum conditions for the transformation of natural triglycerides into fuels [5–12]. It has been stated that the first step of this process is hydrogenation of the triglycerides (saturation of olefinic double bonds), followed by the formation of

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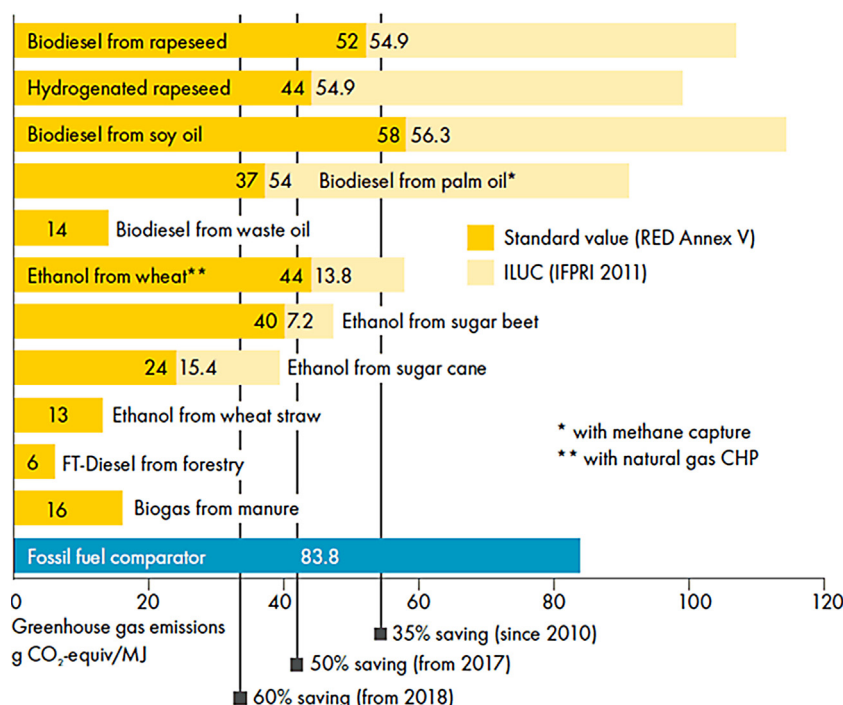


Fig. 1. Greenhouse gas standard values of RED and exemplary ILUC values [1].

various intermediates: carboxylic acids, mono- and diglycerides transformed into alkanes by decarboxylation, decarbonylation and hydrodeoxygenation pathways. Transformation of carboxylic acids into alkanes is accompanied by the production of CO₂, CO and CH₄. Isomerization and cracking of the straight chain also takes place, producing isomerised and light alkanes, respectively. The fatty acids must be converted completely, because any remaining acids would inhibit the isomerization processes [13].

Formation of CO₂ in the decarboxylation reaction is a very important problem, because of hydrocarbon yield and of environmental aspects. CO and CO₂ are partially converted into CH₄ on the hydrogenation catalysts, especially in the case of nickel containing ones. Elimination of CO is particularly important, since it would act there as a catalyst poison [14]. Decarboxylation of fatty acids and their methyl esters have been, for example, investigated also on Pd/C [15–18] and Pt/Al₂O₃ catalysts [19]. It is very important to avoid the reaction of CO₂, e.g. the formation of CH₄ because the increased consumption of hydrogen results in a shortage of it, causing decreased yield of the diesel fuel [20].

A complex conversion in hydrodeoxygenation and decarboxylation of triglycerides can be achieved [5,12,20–22] using well-known hydrodesulfurization (HDS) catalysts; as the sulfided Mo/Al₂O₃ or Ni- or Co-promoted molybdena-alumina (NiMo/Al₂O₃), and CoMo/Al₂O₃) as well as NiW/Al₂O₃, the Ni-promoted, alumina supported tungsten [23]. It is seen, that the extent of CO and CO₂ formation influences the >C=C< hydrogenation and ≥C–C≤ hydrogenolysis reaction. The reaction pathway of the CO formation, is, however not clean. Donnis et al. [20] highlighted that beside hydrogenation and decarboxylation, decarbonylation can also occur, since the split of the carboxyl chain can proceed by two ways. Crocker et al. [24] concluded that the formation ratio of CO₂: CO is generally between 1:2 and 2:1 on different catalysts; namely CO is a primary product, since the reaction equilibrium constant of the reverse water–gas reaction is only 0.04 at the temperature of the experiments (350 °C). On the other hand, Kubička and Kaluža [25] considered only decarboxylation as the primary reaction, concluding that CO was formed by secondary

reactions. The radioactivity of ¹⁴C-labeled methane measured by us cannot be influenced by non-radioactive methane formed by cracking of the unlabeled hydrocarbon chain of the oleic acid-1-¹⁴C, as it (the ¹⁴C labeled methane) was normalized to the radioactivity values of the other labeled participants being present: non converted oleic acid-1-¹⁴C, i.e. ¹⁴COOH, C₁₇H₃₅¹⁴CH₃, ¹⁴CO and ¹⁴CO₂. The aim of our study was the investigation of the deoxygenation mechanism (decarbonylation, decarboxylation) of the acid.

For a more detailed understanding of decarboxylation, decarbonylation and deoxygenation reactions of fatty acids on sulfided Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts we studied the processes with ¹⁴C-labeled oleic acid [oleic acid-1-¹⁴C indicating that the acids were selectively labeled with ¹⁴C only at the COOH groups]. The aim of this study was to obtain some direct information about the activity and selectivity of these two different catalyst samples in the rupture of H₂C–CO, HOC=O and HO–CO bonds in the processes with oleic acid-1-¹⁴C. These catalysts have been selected for this study as their extremely different chemical content serves served to answer, how far this difference is expressed in their interaction with the –COOH group in the oleic acid. Among the aims of these experiments was the determination of the amounts of carbon-like deposits formed on the catalyst samples at these conversions.

A special measurement series have been also carried out with ³⁵S radioisotope-labeled catalyst samples to determine the amount of sulfur, removed from the sulfided samples by oleic acid and/or by the products of its conversion. The experiments have been performed in a dynamic system, as our measurements indicated a substantially higher selectivity of the catalysts in comparison with the hydrotreatment of the oleic acid in pulse system.

2. Experimental

2.1. Procedure and instrumentation, including radioactivity measurements

In Fig. 2 is shown the catalytic microsystem applied for experiments with oleic-acid-1-¹⁴C. The equipment consists of two

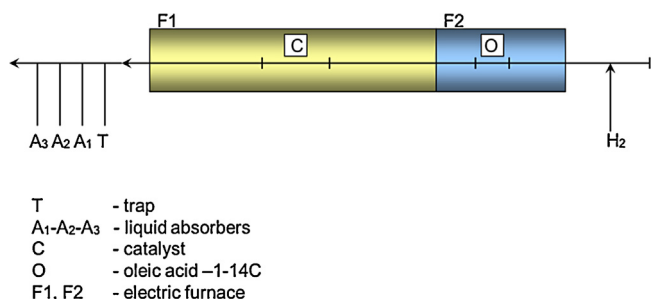


Fig. 2. The schematic presentation of the micro reactor system applied.

precision electric furnaces. The first one is applied for heating 50 mg samples of the sulfided catalyst. The second furnace serves for evaporation of the oleic acid-1- ^{14}C into the stream of hydrogen, taking 5–15 mg portions of oleic acid-1- ^{14}C , and diluted with nonradioactive oleic acid measured in a glass capillary with analytical precision placed into the glass reactor tube. The time of evaporation was 10 min.

The radioactive (labeled with ^{14}C) oleic acid was previously diluted in non-radioactive oleic acid to 11340 dpm/mg of the ARC (American Radiochemical Company) produced oleic acid-1- ^{14}C of 2.035 GBq/mmol specific radioactivity. Thereafter a trap and three liquid absorbers were connected to the reactor system for freezing and absorption of the radioactive side-products formed in the processes of decarboxylation, decarbonylation and deoxygenation. The flow rates of hydrogen have been accepted as the flow rates of the oleic acid on the bases of experiments [26,27], indicating a flow of square reactant pulses in conditions, similar to those applied. These flow rates were 20, 30, and 40 cm^3/min (NTP; this means the indicated volume at 298 K temperature and 101.325 kPa pressure) i.e. 5.01 , 7.52 and 10.03×10^{20} molecules/min, respectively. The unreacted oleic acid-1- ^{14}C , the produced $^{14}\text{CO}_2$ and $\text{RCH}_2^{14}\text{CH}_3$ were frozen, while ^{14}CO and $^{14}\text{CH}_4$ were collected by liquid absorbers. The completeness of absorption of $^{14}\text{CO}_2$, ^{14}CO , $^{14}\text{CH}_4$, and $\text{R-CH}_2^{14}\text{CH}_3$ was controlled by using a second absorber. No radioactivity was present in the second absorber, except of $^{14}\text{CH}_4$ (5%). The radioactivity values represented the amounts of the produced CO , CO_2 , CH_4 , $\text{R-CH}_2\text{CH}_3$ and of the unreacted oleic acid, respectively. Measurements of the radioactivity were carried out in liquid scintillation spectrometer (LSC TriCarb 2800 Perkin Elmer) using solubilisation in liquid scintillator ClinisitolTM (Inst. Isotopes Hung. Acad. Sci.). Previously the quantitative formation of methane, labeled with carbon ($^{14}\text{CH}_4$) has been studied and proved on Ni-catalyst in hydrogen stream at atmospheric pressure [28]. The CH_4 : CO : CO_2 ratio in the gas mixtures determined by the ratio of their radioactivities has been confirmed by comparison with data, determined by measurements with FT-IR. The amount of $\text{R-CH}_2^{14}\text{CH}_3$ formed, was determined only after separation by thin layer chromatography (TLC) from oleic acid-1- ^{14}C . Fig. 3 presents a TLC chromatogram illustrating the separation of $\text{C}_{17}\text{H}_{35}^{14}\text{CH}_3$ from the unreacted oleic-acid-1- ^{14}C . The content of the mobile phase was there Petroleum Ethers and Ethyl Acetate of ratio 4:1; that for the stationary was: Merck Alufolien Silica gel 60.

2.2. Characteristic data of the catalyst samples

Table 1 contains the chemical content and specific surface data for the two commercial catalyst samples, applied in studies of their

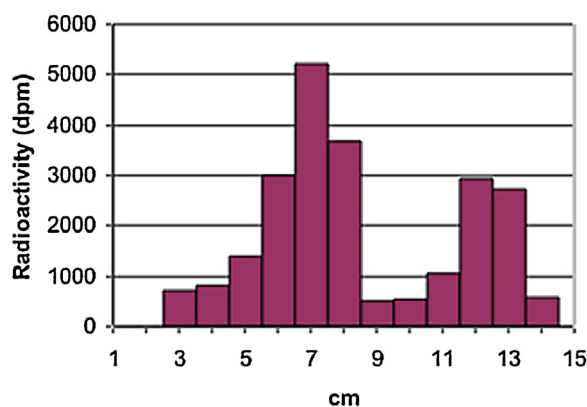


Fig. 3. TLC separation of $\text{C}_{17}\text{H}_{36}^{14}\text{CH}_3$ from the non-reacted oleic acid-1- ^{14}C (2–8.5 cm oleic acid-1- ^{14}C , 11–13 cm $\text{C}_{17}\text{H}_{35}^{14}\text{CH}_3$) Rf: Oleic acid 0.38 $\text{C}_{18}\text{H}_{38}$ 0.77.

catalytic behavior in hydrotreating oleic acid-1- ^{14}C . These data – determined in the Laboratory of Dep. of MOL Hydrocarbon and Coal Processing – indicate substantial differences between the two samples:

- The concentration of tungsten ions is substantially higher in the $\text{NiW}/\text{Al}_2\text{O}_3$ than that of the molybdenum modified with phosphorus in the sample $\text{Mo}/\text{P}/\text{Al}_2\text{O}_3$;
- The $\text{Mo}/\text{P}/\text{Al}_2\text{O}_3$ sample contains phosphorus in order of the amounts of Mo-atoms, whereas the $\text{NiW}/\text{Al}_2\text{O}_3$ sample does not contain any;
- The specific surface area ($306 \text{ m}^2/\text{g}$) is higher by $\sim 75\%$ for the $\text{NiW}/\text{Al}_2\text{O}_3$ sample, than that ($172 \text{ m}^2/\text{g}$) of the other one.

2.3. Presulfidation of the catalyst samples

The catalyst samples were sulfided with H_2S (labeled both with radioactive H_2^{35}S and with a non-labeled one) in a circulation reactor system. The method, applied for sulfidation was described previously [29]. The H_2 : H_2S (or H_2^{35}S) mass ratio was 1:1 and the catalysts were treated for 3 h by circulation with these mixtures at 623 K. The radioactivity of the H_2 : H_2^{35}S mixtures became constant for 60 min, indicating that the equilibrium of the sulfur uptake and that of the $\text{S}_{\text{cat}} \leftrightarrow \text{H}_2^{35}\text{S}$ sulfur exchange was reached. Special measurements, carried out with these and with several other $\text{NiMo}/\text{Al}_2\text{O}_3$ of different Ni: Mo ratio [30] indicated also that this equilibrium has been reached among conditions applied in these experiments.

The determined initial ^{35}S contents of the $\text{Mo}/\text{P}/\text{Al}_2\text{O}_3$ and $\text{NiW}/\text{Al}_2\text{O}_3$ catalysts were 1.12×10^{17} and 16.56×10^{17} S/mg respectively (Table 1). The degrees of sulfidation, – calculated by supposing the formation of MoS_2 and NiWS_2 at treatment with H_2S – were respectively 0.37 and 0.84.

2.4. Determination of the loss of sulfur from presulfided $\text{Mo}/\text{P}/\text{Al}_2\text{O}_3$ and $\text{NiW}/\text{Al}_2\text{O}_3$ catalysts during the hydrotreating process of oleic acid

Nonradioactive oleic acid was flown through the catalyst samples sulfided with ^{35}S for determination of sulfur loss from the catalysts and its temperature dependence under conditions applied

Table 1

The specific surface (S.A.), chemical composition of the catalysts and their irreversible S-uptake.

Catalyst	S.A. m^2/g	Ni at/mg	Mo at/mg	W at/mg	P at/mg	S_{cat}
$\text{Mo}/\text{P}/\text{Al}_2\text{O}_3$	172	–	1.5×10^{17}	–	1.95×10^{17}	1.12×10^{17}
$\text{NiW}/\text{Al}_2\text{O}_3$	305	8.64×10^{17}	–	5.51×10^{17}	–	16.56×10^{17}

Table 2The decrease of $^{35}\text{S}_{\text{cat}}$ content (^{35}S atoms and in %) at hydrotreatment of oleic acid on ^{35}S labeled sulfides.

T °K	Mo/P/Al ₂ O ₃		NiW/Al ₂ O ₃	
	^{35}S at./mg	S%	^{35}S at./mg	S%
573	3.4×10^{15}	3.05	1.9×10^{15}	0.11
593	1.9×10^{15}	1.70	1.8×10^{15}	0.10
613	1.3×10^{15}	1.20	1.4×10^{16}	0.84
633	1.7×10^{15}	1.60	7.7×10^{15}	0.46
653	1.4×10^{15}	1.30	2.3×10^{15}	0.14
673	1.7×10^{15}	1.50	6.6×10^{15}	0.40
Σ	11.4×10^{15}	10.35	34.3×10^{15}	2.05

Initial ^{35}S content of Mo/P/Al₂O₃: $1.12 \times 10^{17}/\text{mg}$; that of NiW/Al₂O₃: $16.56 \times 10^{17}/\text{mg}$

in the experiments for studies of oleic acid conversions. The flow rate of hydrogen in these experiments was 40 NTP/min, the highest one applied in this study of oleic acid treatment. The amounts of the sulfur losses of the catalysts were determined for one sample in these series of experiments in the interval of temperature measuring the radioactivity of the samples treated this way, and using an alkaline absorber for binding of the H_2^{35}S in the process. The measurement method and calculation of these data were detailed previously [29].

Data in Table 2 indicates, that the total loss of the sulfur content during these experiments, provided in the 573–673 K interval of temperature was 11.4×10^{15} and 34.3×10^{15} S/mg for Mo/P/Al₂O₃ and NiW/Al₂O₃, respectively, i.e. 10.18 and 2.07 percents of the sulfur content of the samples. These data indicate that small amounts of sulfur were removed from the catalysts by oleic acid and/or by the products of its conversion: the sulfur losses at one temperature

were 0.1–3% of the original content both on Mo/P/Al₂O₃ and on NiW/Al₂O₃. The ratio of the sulfur losses, related to the S-content was higher from the sulfided Mo/P/Al₂O₃ sample, than those from the NiW/Al₂O₃. This is in agreement with the observed higher ratio of the reversible uptake of sulfur on Mo/P/Al₂O₃ (0.71) [30], than that on the NiW/Al₂O₃ (0.62). The high ratio of the reversible sulfur uptake is presumably connected with a high ratio of sulfur, adsorbed in form of SH [31].

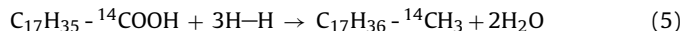
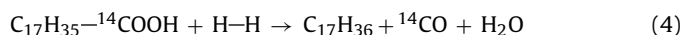
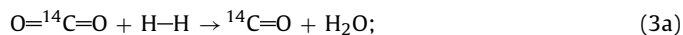
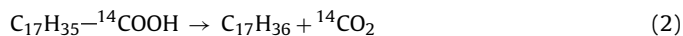
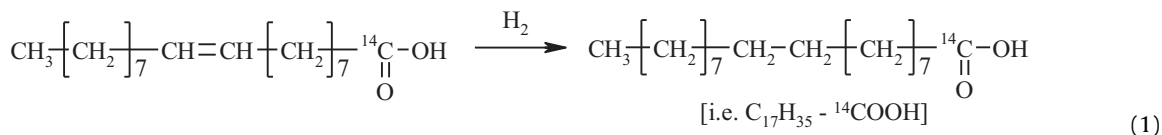
There have been performed special measurements of the radioactivity of the sulfided catalyst samples after their treatment in oleic-acid-1- ^{14}C . The results of these measurements indicated that the radioactivity of the catalysts presented then only 0.1% of the initial radioactivity of the oleic acid injected; no elemental carbon was formed from the carboxyl group practically. It can be stated, that the activity of the catalysts was near to constant among the experimental conditions, as this is important for the comparison of their catalytic properties.

3. Results and discussion

It is well known that numerous vegetable oils contain relatively high amounts of free acid, e.g., oleic acid [32,33]. The fatty acids are the main reaction intermediates in catalytic deoxygenation of the triglycerides, respectively. This indicates that the catalytic

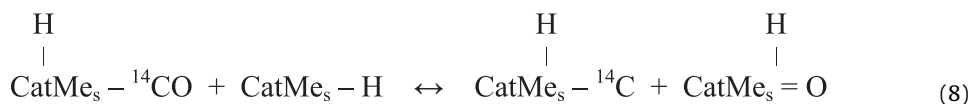
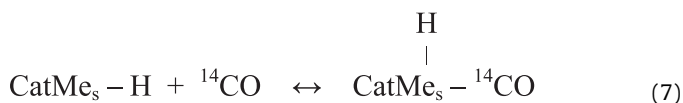
hydrotreating of oleic acid-1- ^{14}C is a very suitable model for the study of oxygen removal in fatty acid conversion and in production of normal alkanes and for the evaluation of the applicability of different catalysts in these processes.

It is evident that the first reaction step is the hydrogenation of the $>\text{C}=\text{C}<$ double bond. $^{14}\text{CO}_2$ can be produced by a unimolecular decarboxylation process [step (2)], resulting in the formation of $\text{C}_{17}\text{H}_{36}$ alkanes by the rupture of the $\text{C}-^{14}\text{CO}$ and $^{14}\text{CO}-\text{H}$ bonds in the $-\text{COOH}$ group. Hydrogen is not required for the production of $^{14}\text{CO}_2$ in this step. Nevertheless, ^{14}CO can be formed by decarbonylation via interaction with hydrogen [step (4)]. The hydrodeoxygenation pathway [step (5)] is a very important one, as the carboxyl group is converted there into an alkane: $\text{C}_{17}\text{H}_{35}^{14}\text{CH}_3$. This observation supports the previous statement [34], namely that the reaction pathway requires the application of bifunctional catalyst for hydrogenation and dehydration reactions:



The accomplished measurements indicate that radioactive compounds containing $\text{C} < 18$ were not found among the products of conversion besides of the $^{14}\text{C}_1$ products formed from $^{14}\text{COOH}$ group.

It is seen from Fig. 4, that there formed on NiW/Al₂O₃ a higher ratio of $^{14}\text{CH}_4$ at the oleic acid-1- ^{14}C conversion. This is undesired from practical (economic) point of view, because the production of methane increases significantly the consumption of hydrogen. This indicates that the hydrotreating catalyst NiW/Al₂O₃ was also active in ^{14}CO hydrogenation. The formation of $^{14}\text{CH}_4$ can be detailed by the following way, in agreement with the mechanism proposed earlier [35]:



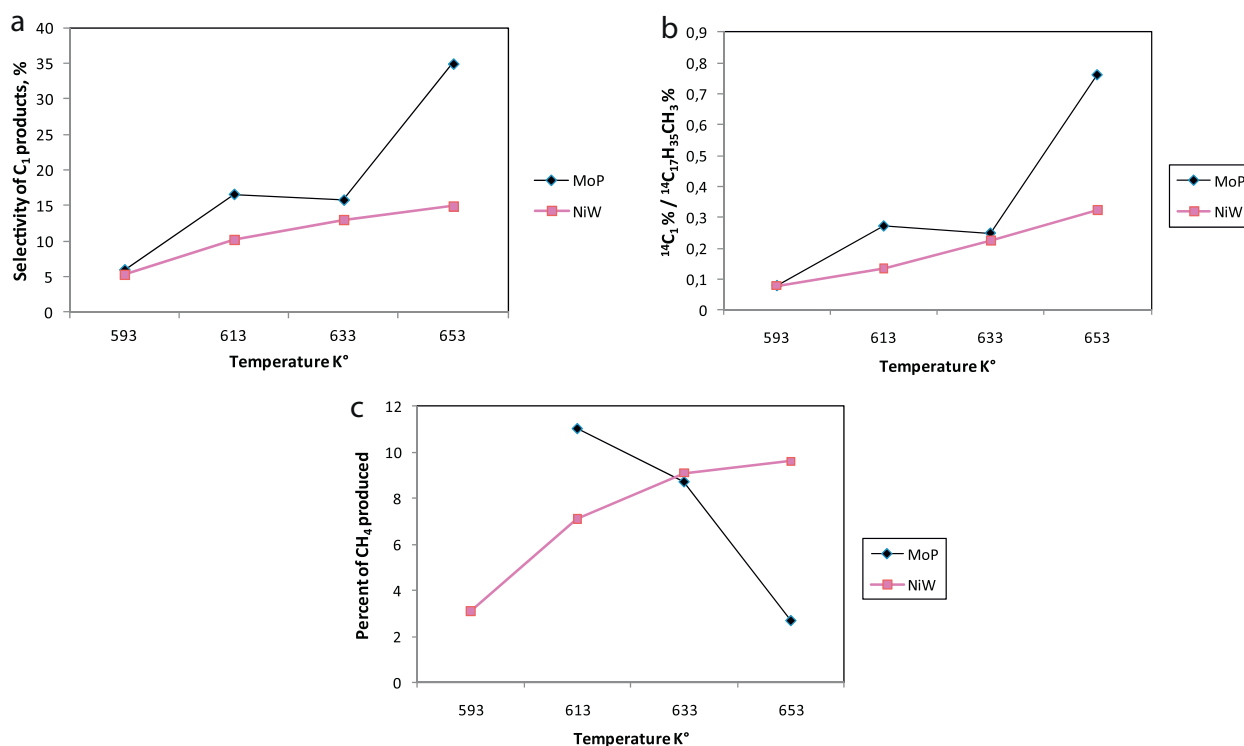
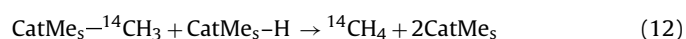


Fig. 4. a. The temperature dependence of $\sum C_1$ percentages separated from ($^{14}\text{COOH}_{\text{conv.}} + ^{14}\text{COOH}_{\text{nonconv.}}$) at oleic acid -1- ^{14}C conversion on the sulfided Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts. b. The temperature dependence of the $\sum ^{14}\text{C}_1\% / \text{C}_{17}\text{H}_{35}^{14}\text{CH}_3\%$ ratios (i.e. the $\sum ^{14}\text{C}_1 / \text{C}_{17}\text{H}_{35}^{14}\text{CH}_3$ selectivity ratios) among the products of the oleic acid -1- ^{14}C conversion on the sulfided Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts. c. The temperature dependence of the values of CH₄ selectivity in % among the products of the oleic acid-1- ^{14}C conversion on the sulfided Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts.



The equations represent the dissociative adsorption of H₂ and a molecular one for ^{14}CO , respectively. The atoms, formed at dissociation of ^{14}CO react with adsorbed hydrogen in the next steps resulting in a stepwise formation of $^{14}\text{CH}_4$.

This cited mechanism does not exclude the stepwise hydrogenation of the double bonds in the CO₂ followed by hydrogenolysis of the σ C–C bonds by the adsorbed hydrogen.

There have been performed special measurements of the radioactivity of the catalyst samples after their treatment in oleic acid-1- ^{14}C . The results of these measurements indicated that the radioactivity of the catalysts presented then only 0.1% of the initial radioactivity of the oleic acid injected; no elemental carbon was formed from the carboxyl group practically. The small decrease of the catalytic activity was presumably a consequence of the decrease of the catalyst S-content, presented before in Table 2. It can be stated, that the activity of the catalysts is near to constant in the experimental conditions applied, as this is important for the comparison of their catalytic properties. In Tables 3 and 4 the conversion data are presented, as determined at three different flow rates for the Mo/P/Al₂O₃ and NiW/Al₂O₃ catalyst samples at T = 633 K. These data raise the question: how can be predicted the conversion rates for different flow rates of the reactants. Data, presented on Fig. 5

indicate a correlation between the degree of conversion (y) and the flow rate of the oleic acid (F):

$$F \ln 1/(1-y) = \alpha + \beta Fy \quad (13)$$

$$\alpha = kb_1/(1 + \sum b_i); \quad \beta = (b_1 + \sum b_i)/\sum b_i \quad (14)$$

where k means the constant of the conversion rate; b_1 and b_i are the adsorption equilibrium constants of oleic-1- ^{14}C acid and of the products of its conversion, respectively.

Eq. (13) has been applied earlier in a high number of studies [36] including the conversion (dehydrogenation and dehydration) of alcohols, hydrogenolysis and cracking of hydrocarbons [37,38].

The substantially higher β value, indicated in Fig. 5a for Mo/P/Al₂O₃ (1.8796) in comparison with that for NiW/Al₂O₃ (0.9973) explains that the HDO reaction rates on Mo/P/Al₂O₃ are higher than those at the $F < 20 \text{ cm}^3/\text{min}$, in spite of the fact that the α value for NiW/Al₂O₃ is higher (~ 16) than that for Mo/P/Al₂O₃ (~ 3).

The $F \ln 1/(1-y)$ vs. Fy graphs in Fig. 5 prove that this equation is suitable to predict the oleic-1- ^{14}C conversion. There are definite differences between the data, characterizing the total oleic acid conversion on the two samples.

The substantially higher value of α for NiW/Al₂O₃ ($\sim 16 \text{ cm}^3/\text{min}$) in comparison with that for Mo/P/Al₂O₃ ($3.1 \text{ cm}^3/\text{min}$) indicates a substantially higher rate constant of the oleic acid-1- ^{14}C conversion on NiW/Al₂O₃. Data in Tables 3 and 4 indicate that the degree of conversion of the carboxyl group

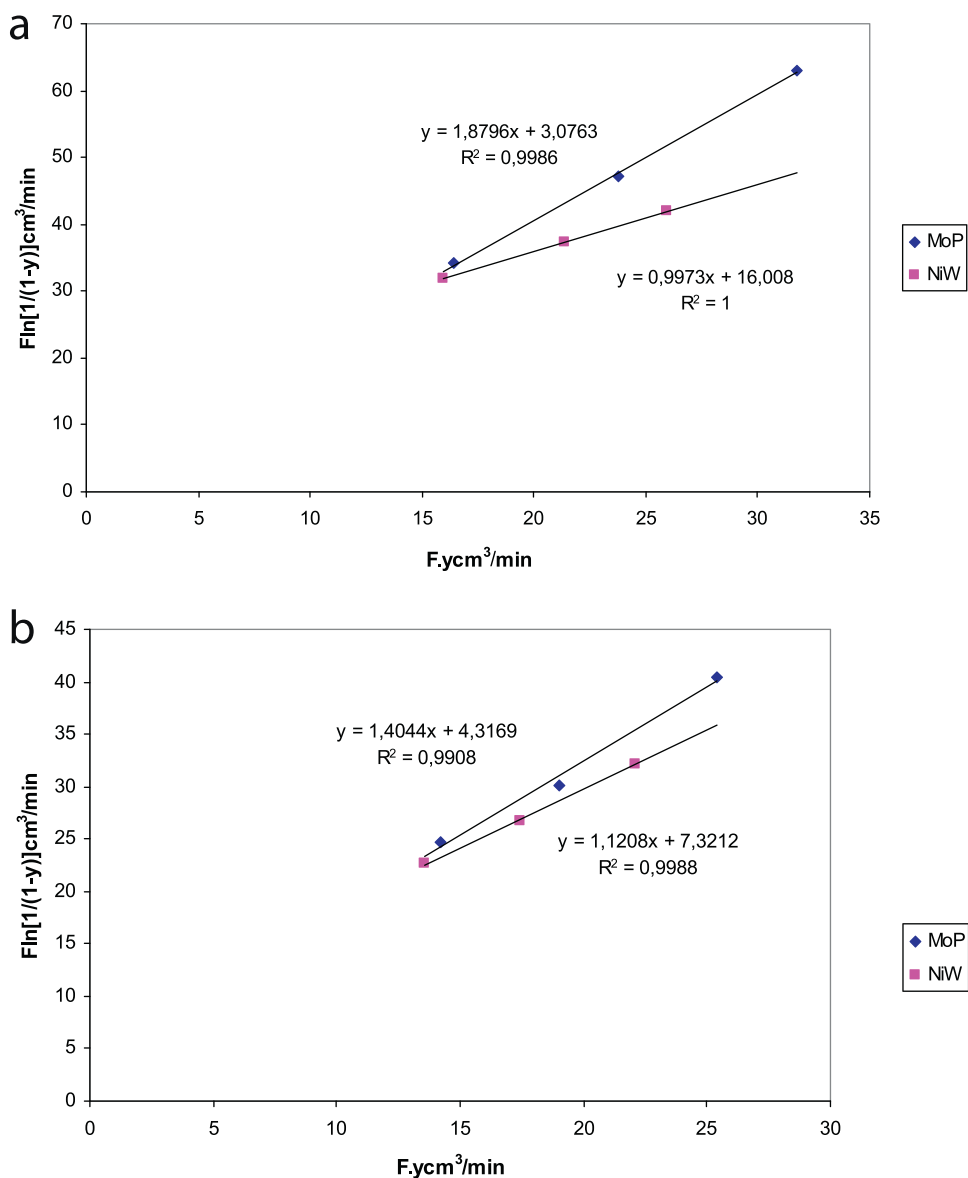


Fig. 5. a. The dependence of the degree of the total oleic-acid-1- ^{14}C conversion (y) on the flow rate on Mo/P/Al $_2$ O $_3$ and NiW/Al $_2$ O $_3$. b. The dependence of the degree of the oleic-acid-1- $^{14}\text{C} \rightarrow \text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3$ conversion (y) on Mo/P/Al $_2$ O $_3$ and NiW/Al $_2$ O $_3$ on the flow rate.

and the amounts of the $\sum \text{C}_i$ products are nearly constant in conversion over Mo/P/Al $_2$ O $_3$.

Different from this, a definite decrease of the conversion percentage is observed over the NiW/Al $_2$ O $_3$ sample at increasing flow rate. The differences in the sum of C_i products ($\sum \text{C}_i$) are very limited also at increasing flow rate over the NiW/Al $_2$ O $_3$ sample. Different from this, the correlation $^{14}\text{CO} : ^{14}\text{CO}_2 : ^{14}\text{CH}_4$ depends

definitely on the flow rate of hydrogen, and—with one exception – $^{14}\text{CH}_4 > ^{14}\text{CO}_2 > ^{14}\text{CO}$. This exception – $\text{CO}_2 > \text{CH}_4 > \text{CO}$ – was observed in the case of application of Mo/P/Al $_2$ O $_3$ at a flow rate of 20 cm^3/min . In this case the maximal ratio of $\text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3$ was observed, the main product of the $-\text{COOH}$ conversion of oleic acid.

In Tables 5 and 6 the products of oleic acid-1- ^{14}C conversion are presented, as determined at different temperatures and at

Table 3

The conversion of oleic acid-1- ^{14}C carboxyl group^a on sulfided Mo/P/Al $_2$ O $_3$; distribution of C_1 products at different flow rates of hydrogen; $T = 633 \text{ K}$.

F NTP cm^3/min	$-\text{}^{14}\text{COOH}_{\text{conv.}}$		$\text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3$		^{14}CO		$^{14}\text{CO}_2$		$^{14}\text{CH}_4$		$-\text{}^{14}\text{COOH}_{\text{nonconv.}}$	
	%	molec./s mg	%	molec./s mg	%	%	%	%	%	%	%	molec./s mg
20	81.9	1.67×10^{17}	71.0	1.45×10^{17}	1.8	5.5	3.6	18.1	3.69×10^{16}			
30	79.2	9.67×10^{16}	63.4	7.74×10^{16}	0.3	6.8	8.7	20.8	2.54×10^{16}			
40	79.3	9.68×10^{16}	63.6	7.76×10^{16}	0.0	7.0	8.7	20.7	2.53×10^{16}			

^a $-\text{}^{14}\text{COOH}_{\text{conv}}$ and $-\text{}^{14}\text{COOH}_{\text{nonconv}}$ and $\text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3$: the amounts of the converted, non converted carboxyl groups and the produced $\text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3$ respectively in conversion of oleic acid-1- ^{14}C ; ^{14}CO %, $^{14}\text{CO}_2$ % and $^{14}\text{CH}_4$ % indicate respectively the percentages of the products in conversion of oleic acid-1- ^{14}C conversion.

$^{14}\text{CO}\% + ^{14}\text{CO}_2\% + ^{14}\text{CH}_4\% + \text{C}_{17}\text{H}_{35}\text{-}^{14}\text{CH}_3\% = -\text{COOH}_{\text{conv.}}\%$.

The mass of the catalyst sample: 50 mg.

Table 4

The conversion of oleic acid-1-¹⁴C carboxyl group^a on sulfided NiW/Al₂O₃; distribution of C₁ products at different flow rates (F) of hydrogen; T = 633 K.

F NTP cm ³ /min	— ¹⁴ COOH _{conv.}		C ₁₇ H ₃₅ ¹⁴ CH ₃		¹⁴ CO	¹⁴ CO ₂	¹⁴ CH ₄	— ¹⁴ COOH _{nonconv.}	
	%	molec./s mg	%	molec./s mg	%	%	%	%	molec./s mg
20	79.7	1.63 × 10 ¹⁷	67.7	1.38 × 10 ¹⁷	1.3	3.6	7.1	20.3	4.15 × 10 ¹⁶
30	71.2	8.69 × 10 ¹⁶	58.2	7.10 × 10 ¹⁶	1.8	2.1	9.1	28.8	3.52 × 10 ¹⁶
40	64.9	7.92 × 10 ¹⁶	55.3	6.75 × 10 ¹⁶	1.2	1.3	7.1	35.1	4.28 × 10 ¹⁶

^a —¹⁴COOH_{conv.} and —¹⁴COOH_{nonconv.} and C₁₇H₃₅¹⁴CH₃: the amounts of the converted, non converted carboxyl groups and the produced C₁₇H₃₅¹⁴CH₃ respectively in oleic acid-1-¹⁴C; %, ¹⁴CO %, ¹⁴CO₂ % and ¹⁴CH₄ % indicate the percentages of the respective products of oleic acid-1-¹⁴C conversion.

• ¹⁴CO % + ¹⁴CO₂ % + ¹⁴CH₄ % + C₁₇H₃₅¹⁴CH₃ % = —COOH_{conv.} %

• The amount of catalyst: 50 mg.

Table 5

The temperature dependence of the oleic acid-1-¹⁴C carboxyl group conversion on sulfided Mo/P/Al₂O₃; the distribution of ¹⁴C₁ and C₁₇H₃₅¹⁴CH₃ products^a; F = 30 NTPcm³/min.

T K	— ¹⁴ COOH _{conv.}		C ₁₇ H ₃₅ ¹⁴ CH ₃		¹⁴ CO	¹⁴ CO ₂	¹⁴ CH ₄	— ¹⁴ COOH _{nonconv.}	
	%	molec./s.mg	%	molec./s.mg	%	%	%	%	molec./s.mg
593	81.9	1.00 × 10 ¹⁷	76.0	9.28 × 10 ¹⁶	0.4	5.5	<0.1	18.1	2.21 × 10 ¹⁶
613	77.6	9.47 × 10 ¹⁶	61.0	7.44 × 10 ¹⁶	0.1	5.5	11.0	22.4	2.73 × 10 ¹⁶
633	79.2	9.67 × 10 ¹⁶	63.4	7.74 × 10 ¹⁶	0.3	6.8	8.7	20.8	2.54 × 10 ¹⁶
653	80.4	9.82 × 10 ¹⁶	45.8	5.59 × 10 ¹⁶	<0.1	32.1	2.7	19.6	2.35 × 10 ¹⁶

^a —¹⁴COOH_{conv.} and —¹⁴COOH_{nonconv.} and C₁₇H₃₅¹⁴CH₃: the amounts of the converted, non converted carboxyl groups and the produced C₁₇H₃₅¹⁴CH₃ respectively in conversion of oleic acid-1-¹⁴C; ¹⁴CO %, ¹⁴CO₂ % and ¹⁴CH₄ % indicate respectively the percentages of the products in conversion of oleic acid-1-¹⁴C conversion.

¹⁴CO % + ¹⁴CO₂ % + ¹⁴CH₄ % + C₁₇H₃₅¹⁴CH₃ % = —COOH_{conv.} %.

The mass of the catalyst sample: 50 mg.

30 cm³/min flow rates. The maximum degrees of conversion values were near to equal, 82.5 and 85.9% for Mo/P/Al₂O₃ at 593 K and NiW/Al₂O₃ at 613 K, respectively. No significant temperature dependence of the conversion on the Mo/P/Al₂O₃ was observed, whereas the data in Table 6 indicated a definite effect of the temperature on the conversion over NiW/Al₂O₃. This difference in the temperature dependences of the oleic acid-1-¹⁴C conversion between the two catalysts indicates – similarly to the kinetic data – definite differences in their catalytic behavior in spite of the nearly equal maximum conversions.

It is seen from the data in Tables 5 and 6 that C₁₇H₃₅¹⁴CH₃ was the main product of decarboxylation on both catalysts. The products CO₂ and CO were radioactive. ¹⁴CH₄ was also found in this process, formed evidently by hydrogenation of ¹⁴CO₂ and ¹⁴CO. No another radioactive gas phase compound was present among the reaction products. The sum of the ratios of the C₁ products (Σ¹⁴C₁) was substantially lower among the products of decarboxylation than that of the C₁₇H₃₅¹⁴CH₃. The increase of Σ¹⁴C₁ with temperature (Fig. 4a) indicates a definitely higher energy barrier of the hydrogenolysis of the >C—COOH bond, than that of the formation of C₁₇H₃₅¹⁴CH₃. The ΣC₁/C₁₇H₃₅¹⁴CH₃ ratio increases with temperature on both catalysts, as shown in Fig. 4b.

The formation of ¹⁴C-labeled methane was not observed practically at 593 K, and methane appeared at 613 K and its ratio decreased at the conversion on Mo/P/Al₂O₃ at higher temperature. Different from that, ¹⁴CH₄ increased on NiW/Al₂O₃ as seen from data in Table 6 and represented in the Fig. 4c. This is a consequence

of the higher hydrogenation activity of the Ni content of this catalyst.

The higher energy barrier for hydrogenolysis of the >C—COOH bond strength (Q_{C-C}) of 345 kJ in comparison with that of the formation of C₁₇H₃₅¹⁴CH₃ via the rupture of the >C—O or —O—H bonds (Q_{C-O} and Q_{O-H}) of higher strengths (357 and 462 kJ respectively) in —COOH required for production of C₁₇H₃₅¹⁴CH₃ [39] is connected presumably with the strengths of interaction between the catalyst and the atoms of reacting molecules, participating in the conversions. The expression of the energy barriers (E_{XY}) for the rupture of these bonds [39]:

$$E_{CC} = Q_{C-C} - 2Q_{C-Cat}; E_{C-O} = Q_{C-O} - (Q_{C-Cat} + Q_{O-Cat});$$

$$E_{O-H} = Q_{O-H} - (Q_{O-Cat} + Q_{H-Cat})$$

It follows from this that the low ratio of the Σ¹⁴C₁ products and the difference in temperature dependence of the two conversions (the presumably higher energy barrier of the C—C bond rupture) should be the consequence of the substantially lower strength of the C—catalyst bond (Q_{C-Cat}) than that of the O—Cat (Q_{O-Cat}) and H—Cat (Q_{H-Cat}), as observed for a high number of catalysts, including MoS₂ and WS₂ [37].

The comparison of data in Tables 5 and 6 indicates that the maximum values of the conversion were reached at 613 and 593 K by NiW/Al₂O₃ and Mo/P/Al₂O₃, respectively. The amount of gas products was not too high at maximum —¹⁴COOH conversion on

Table 6

The temperature dependence of the oleic acid-1-¹⁴C carboxyl group conversion on sulfided NiW/Al₂O₃ the distribution of C₁₇H₃₅¹⁴CH₃ and ¹⁴C₁ products^a; F = 30 NTPcm³/min.

T K	— ¹⁴ COOH _{conv.}		C ₁₇ H ₃₅ ¹⁴ CH ₃		¹⁴ CO	¹⁴ CO ₂	¹⁴ CH ₄	— ¹⁴ COOH _{nonconv.}	
	%	molec./s mg	%	molec./s mg	%	%	%	%	molec./s mg
593	72.4	8.84 × 10 ¹⁶	67.1	8.19 × 10 ¹⁶	0.7	1.5	3.1	27.6	3.37 × 10 ¹⁶
613	85.7	1.05 × 10 ¹⁷	75.5	9.25 × 10 ¹⁶	1.2	1.9	7.1	14.3	1.75 × 10 ¹⁶
633	71.1	8.68 × 10 ¹⁶	58.1	7.09 × 10 ¹⁶	1.8	2.1	9.1	28.9	3.53 × 10 ¹⁶
653	60.9	7.44 × 10 ¹⁶	46.0	5.62 × 10 ¹⁶	1.9	3.4	9.6	39.1	4.78 × 10 ¹⁶

^a —¹⁴COOH_{conv.} and —¹⁴COOH_{nonconv.} and C₁₇H₃₅¹⁴CH₃: the amounts of the converted, non converted carboxyl groups and the produced C₁₇H₃₅¹⁴CH₃ respectively in conversion of oleic acid-1-¹⁴C; ¹⁴CO %, ¹⁴CO₂ % and ¹⁴CH₄ % indicate respectively the percentages of the products in conversion of oleic acid-1-¹⁴C conversion.

¹⁴CO % + ¹⁴CO₂ % + ¹⁴CH₄ % + C₁₇H₃₅¹⁴CH₃ % = —COOH_{conv.} %.

The mass of the catalyst sample: 50 mg.

NiW/Al₂O₃, and increased with temperature. At the maximum of the –¹⁴COOH conversion on Mo/P/Al₂O₃ (593 K) the amount of the remaining gas products was lowest (Table 5). In this regard, the Mo/P/Al₂O₃ has advantage over NiW/Al₂O₃.

Only the *n*-octadecane was radioactive among the hydrocarbons produced at hydrotreatment (Figure 3); this indicates that both catalysts were active in hydrodeoxygenation. Hence, these experimental results could verify the following – suggested previously [25,39,40] – reaction pathway of oleic acid-1-¹⁴C conversion over sulfided catalysts.

4. Conclusions

Decarboxylation, decarbonylation and hydrodeoxygenation pathways of oleic acid over Mo/P/Al₂O₃ and NiW/Al₂O₃ catalysts were studied in a microcatalytic system applying oleic acid-1-¹⁴C as the model compound. It was stated that only CO, CO₂, and CH₄ were radioactive among the gas products of conversion of oleic acid-1-¹⁴C. The carboxyl group of this compound was converted by hydrodeoxygenation pathway into a radioactive alkane: C₁₈H₃₈. There was not observed any radioactivity among the products with a lower number of carbon atoms (e.g. 5–8) formed as products of cracking or hydrogenolysis. This indicates that no interaction took place between the gas and cracking products. The C₁₈H₃₈ alkane – formed in hydrodeoxygenation pathway – was not cracked. ¹⁴CO and ¹⁴CO₂ were converted partly into ¹⁴CH₄ and the extent of this process was higher on NiW/Al₂O₃ than on the Mo/P/Al₂O₃ catalyst. That means that more hydrogen is required for hydrotreating of vegetable oils on the NiW/Al₂O₃ catalyst in comparison with Mo/P/Al₂O₃. The ratio of $\sum C_1$ production was lower, and the energy barrier of the $\sum C_1$ production was higher than the energy barriers of the C₁₈H₃₈ production. The decrease of the sulfur content of the sulfided Mo/P/Al₂O₃ was somewhat higher than that of NiW/Al₂O₃. This, however, influenced considerably the catalytic activity only over longer periods. Note that in the case of industrial application, few hundred mg/kg of easily disintegrating sulfur compound is mixed to the feedstock to sustain the sulfided state of catalyst.

Based of these experiments it should be stated that the radioactive tracer method detailed here, is suitable for characterizing of the catalyst samples and optimization of the reaction pathway in the hydrotreating of natural triglycerides.

Acknowledgements

One of the authors Tamás Ollár participated in the experiments, serving a significant part of this research in the frames of TÁMOP 4.2.4. A/2-11-1-2012-0001 National Excellence Program–Elaborating and operating an inland student and researcher personal support system convergence program”. The project was subsidized by the European Union and co-financed by the European Social Fund. This work was supported by the

European Union and co-financed by the European Social Fund in the frame of the TÁMOP-4.2.1/B-09/1/KONV-2010-0003 and TÁMOP-4.1.1.C-12/1/KONV/2012-0017 projects.

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